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THE X-IRRADIATION OF HYDRAZINE AND 1,1-DIMETHYLHYDRAZINE

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ABSTRACT

Hydrazine and 1,1-dimethylhydrazine were irradiated at room temperature in both the liquid and the vapor phase with 0.1 to 1.0 Angstrom X-rays at intensities of 1×10^2 to 1×10^3 roentgens per minute and with total doses up to 2.3×10^6 rads. This resulted in 0.3- to 31-percent decomposition with decreasing sensitivity to X-radiation as follows: hydrazine vapor, 1,1-dimethylhydrazine vapor, 1,1-dimethylhydrazine liquid, and hydrazine liquid.


INTRODUCTION

This study is a continuation (ref. 1) of an effort to determine the effects of ionizing radiation on the space storability of chemical rocket propellants. The investigation was limited to a survey of the effects of X-rays (0.1 to 1.0 A) on liquid and vapor samples of hydrazine and 1,1-dimethylhydrazine (UDMH) in borosilicate glassware at room temperature and at intensities of 1.0×10^2 to 1.0×10^3 roentgens per minute. Dose-damage relations were determined for the radiation decomposition of the two phases of both compounds. Information was also obtained concerning the dependence of the hydrazine-vapor decomposition on surface area.

APPARATUS AND PROCEDURE

Starting materials were 99.9-percent pure and were obtained from

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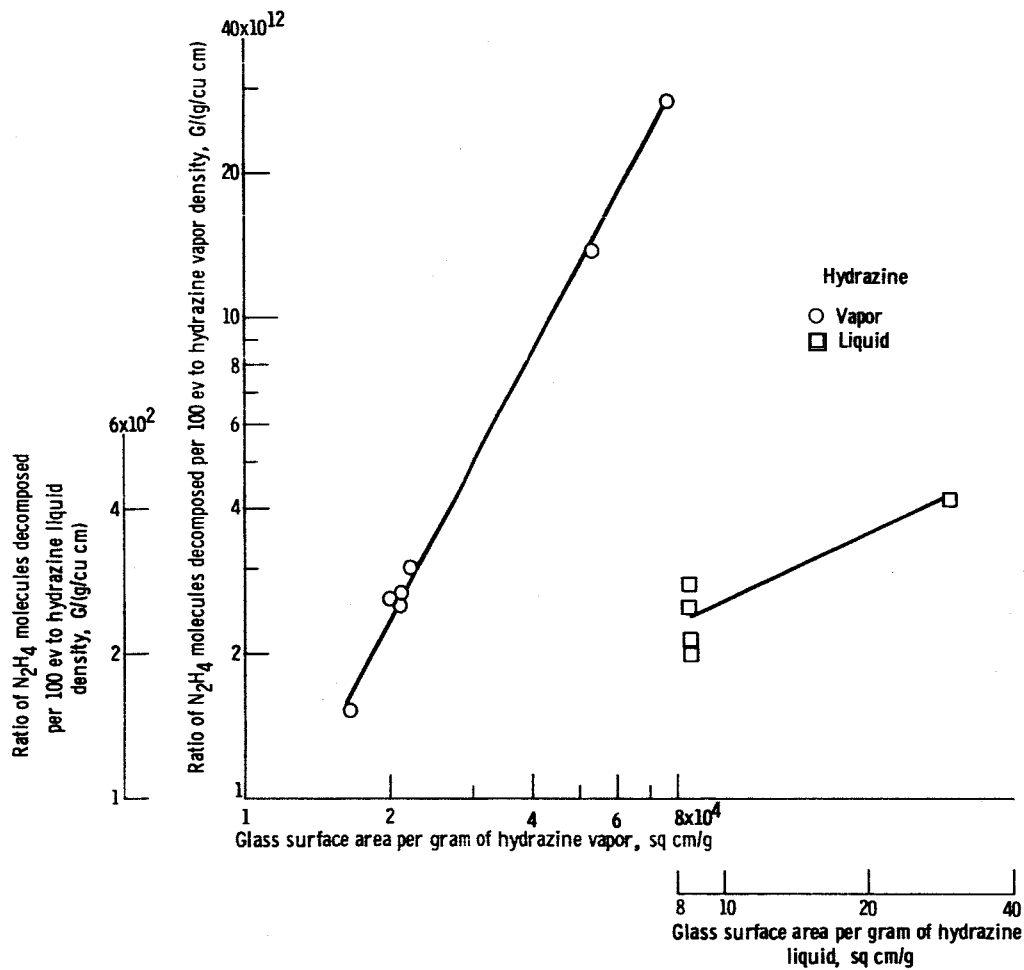


Figure 4. - Effect of surface area on hydrazine decomposition.

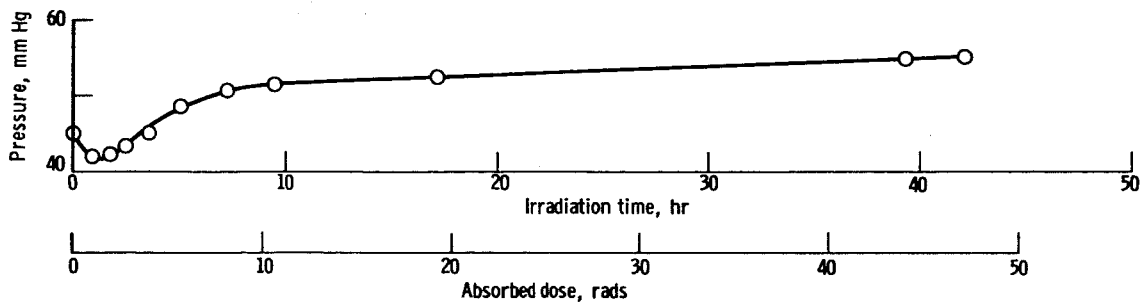


Figure 5. - The X-irradiation of 1,1-dimethylhydrazine vapor. Sample weight, 0.9 gram; dose rate, 1000 rads per minute.

commercial products by dehydration over calcium hydride and low temperature bulb-to-bulb fractionation as described in reference 2. Freshly distilled products were used for each radiation experiment. Irradiations were conducted in sealed borosilicate glassware. Gas cells (fig. 1(a)) were spherical and of 1- or 2-liter capacity; liquid cells (fig. 1(b)) were constructed from 8-millimeter-inside-diameter glass tubing and had capacities of approximately 10 milliliters. Both liquid and gas cells were provided with side arms to permit the introduction of the sample and the transference of irradiation products from the cell to the vacuum system. In addition, gas cells were provided with a pressure transducer to follow pressure changes during the irradiation and a U-shaped trap for condensing the contents of the cell.

The glassware was cleaned with a sulfuric-nitric acid mixture, rinsed with tap and distilled water, and oven dried. Irradiation cells were degassed at 10^{-6} millimeter of mercury and 300° C and charged with a known quantity of sample. Liquid nitrogen was used to freeze the sample while the cell was sealed off and removed from the vacuum line. The liquid cell was placed in a bored lead brick that contained a port on the front face that was continuous with the bore (fig. 1(b)). In this manner, approximately half of the liquid was exposed to primary X-radiation. The entire gas cell was exposed to the beam while a 1/2-inch lead shield protected the pressure transducer. Borosilicate-glass tubing (1.72-mm O.D., 20-mm length, and 0.2-mm wall) was inserted into the gas cell to provide additional surface as was required.

The X-radiation was provided by a tungsten-target generator operating at 300 kilovolts and 6 to 8 milliamperes. Intensities in the range 1×10^2 to 1×10^3 roentgens per minute were used.

In order to confirm that the radiation intensity was constant, the dose rate was monitored continuously with a roentgen rate meter which was equipped with a probe that was covered with a borosilicate-glass thimble of the same thickness as the irradiation cell wall. This probe was placed next to the liquid samples and at the spherical surface nearest the X-ray port for gas samples. The absorbed radiation dose was determined by first conducting ferrous sulfate dosimetry in cells having the same dimensions as the radiation cells ($\text{Fe}^{+2} \rightarrow \text{Fe}^{+3}$, $G = 15.5 \pm 0.4$ where G is the number of ferrous ions converted to ferric ions per 100 ev of absorbed energy) by the method of reference 3 and then by multiplying the result by the ratio of the electron density of the irradiated compound to the electron density of the ferrous sulfate solution.

An indication of the rates of degradation in the vapor-phase irradiations was obtained from the pressure-time traces; however, most of the data were obtained from chemical analyses performed within 1/2 hour after absorption of the predetermined doses. Liquid samples were first frozen in liquid nitrogen, and the permanent gases, nitrogen and hydrogen, were pumped off and analyzed by gas chromatography and mass spectroscopy. These samples were then roughly fractionated by being passed through a series of traps maintained at different reduced temperatures. The contents of each trap were analyzed by infrared spectroscopy or gas chromatography. Retained samples of many of the fractions were sealed off in glass ampoules and stored at room temperature. The irradiated vapor samples were first frozen in liquid nitrogen and the permanent gases were pumped off. They were then analyzed by infrared spectroscopy without further fractionation.

RESULTS AND DISCUSSION

Data from the X-irradiation of hydrazine and 1,1-dimethylhydrazine are summarized in tables I and II. These and other results are considered in the following sections.

X-Irradiation of Hydrazine

Typical results for the X-irradiation of hydrazine are given in table I. The effect of dose rate is considered first. Two 0.025-gram samples of vapor (experiments 6 and 12) were irradiated at 380 and 38 roentgens per minute, respectively, to a total dose absorption of 13 rads, and a similar extent of decomposition (~3 percent) was observed for both samples. The G values and the ratios of nitrogen to hydrogen were also the same for the two runs. Similarly, two 0.9-gram liquid samples (experiments 4 and 5) were exposed to 0.5×10^3 and 1.0×10^3 roentgens per minute, respectively, to total dose absorptions of 9.5×10^5 rads per which about 0.9-percent decomposition was observed. Again the G values and ratios of nitrogen to hydrogen were the same. Therefore, over the range of X-ray doses absorbed, the radiation dose rate does not affect the net decomposition for the same total absorbed dose, all other conditions remaining constant.

A plot (fig. 2) of pressure against absorbed dose shows that there is an initial nonlinear period in the decomposition of hydrazine vapor; however, this initiation period of about 2 to 4 hours is relatively short compared to the total irradiation times in excess of 25 hours. After the initiation process, the pressure, and therefore presumably the percent decomposition, of the vapor increased linearly with absorbed dose. As shown in figure 3(a), the percent decomposition of liquid hydrazine also increased proportionally

to the total dose. The change in decomposition of hydrazine vapor with dose is shown in figure 3(b).

In the hydrazine experiments the absorbed dose was about 10^5 times greater in the liquid than in the vapor phase for approximately the same intensity and time of exposure. The calculated G values show that the decomposition per rad absorbed was about 10^5 times greater in the vapor phase, depending on the surface area and the pressure of the vapor.

Some work done was aimed at determining the effects of surface on the decomposition of hydrazine. This work was somewhat complicated because glass is activated by X-radiation, and the rate of decomposition is higher in irradiated glassware than in new glassware. Borosilicate glass turns dark brown under X-rays and, while part of this color bleaches out after exposure, most of the tint is permanent and can only be removed by fusing the glassware. Active sites on the surface of the tinted glass may play an important role in sustaining chemical reactions. In any case, reproducible results could only be obtained after the glass was irradiated by 2×10^6 roentgens, and the data reported herein were obtained after such treatment.

The effect of surface on the vapor-phase decomposition is shown in experiments 6 through 12 of table I and is plotted in figure 4. Experiments 6, 8, and 9, were identical except that in the last two experiments the cell was packed with capillary borosilicate-glass tubing to increase the surface area. In the other experiments, cells of larger and smaller volume were used, and the sample size, the absorbed dose, and the dose rate were different. Figure 4 shows that the results fit an equation of the form

$$G = C_p \left(\frac{S}{m} \right)^n$$

where

- G number of molecules of sample decomposed per 100 electron volts of absorbed energy
- ρ density, g/cu cm
- S glass surface, sq cm
- m sample weight, g
- n, C constants

For hydrazine vapor, the exponent n is approximately 1.9. The data for liquid hydrazine are much more limited, but when also plotted in figure 4, indicate a much smaller exponent, approximately 0.6. Once reaction started, the surfaces were covered with small bubbles. It might be expected that a much higher rate would then be observed since the reaction rate would be higher in the gas phase than in the liquid phase. Possibly active intermediates are quenched in the liquid phase.

The irradiation of hydrazine (N_2H_4) formed, in addition to nitrogen, hydrogen, and ammonia, small amounts of materials having higher molecular weights than hydrazine, as was shown by gas chromatography. These materials were unstable and were best observed by freezing out the radiation products in liquid nitrogen prior to turning off the X-rays.

X-Irradiation of 1,1-Dimethylhydrazine

Data for the liquid- and vapor-phase irradiations of UDMH are given in table II. All vapor-phase experiments were performed in X-ray aged, 2-liter flasks. The effect of varying surface area was not studied. The percent liquid decomposed was again proportional to the absorbed dose (fig. 3(c)). The effect of the dose on vapor decomposition is shown in figure 3(d).

As with N_2H_4 , the decomposition of UDMH per rad absorbed is several

orders of magnitude higher in the vapor than in the liquid phase. A pressure-dose plot for the vapor-phase reaction is shown in figure 5. The initial reduction in pressure indicates that a polymerization reaction and possibly some condensation occurs in the early stages of the X-irradiation. This initial reduction is followed by a relatively rapid increase in pressure and then by a slower steady pressure increase. Unstable compounds were found in samples taken during the time of minimum pressure. These compounds decomposed in 5 to 20 minutes at room temperature to hydrogen, nitrogen, dimethylamine, and traces of other components.

All the irradiated UDMH samples produced ammonia, dimethylamine, nitrogen, hydrogen, and other products. When the product from experiment 13 (table II) was separated into seven fractions by a two-stage trap-to-trap fractionation, it was found to contain hydrogen, nitrogen, ammonia, methylamine, dimethylamine, undecomposed UDMH, and three probably different, unstable components. The fractions containing these unstable components decomposed in about 2 months at room temperature to form, in part, small quantities of viscous liquids with very low vapor pressures. The latter liquids were not volatile at 10^{-6} millimeters of mercury and room temperature. One of these residues was dark blue initially, turned red on pumping, but reverted to dark blue on standing; another residue was brownish red.

A significant aspect of the irradiation of hydrazine and UDMH is the possibility of postirradiation reactions induced by the primary radiation effect. The phenomenon of postirradiation change was most pronounced with UDMH vapor. Similar effects, though small, were observed with the liquids. Formation of viscous products of the kind described was not observed with hydrazine, although transient products of molecular weights greater than hydrazine were suspected.

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3. Weiss, J., Allen, A. O., and Schwarz, H. A.: Use of the Fricke Ferrous Sulfate Dosimeter for Gamma-Ray Doses in the Range 4 to 40 kr. Proc. Int. Conf. on Peaceful Uses of Atomic Energy, vol. 14, 1956, pp. 179-181.

TABLE I. - X-IRRADIATION OF HYDRAZINE^a

Experiment	Sample weight, g	Dose rate (meter) r/min	Dose rate (ferrous sulfate solution) r/min	Irradiation time, hr	Dose absorbed by sample, rads	N ₂ H ₄ decomposed, percent	Volume N ₂ +H ₂ formed (STP) ^b , ml	Ratio of nitrogen to hydrogen, N ₂ /H ₂	Values of G for decomposition of hydrazine	Sample volume, cu cm	Cell surface area, sq cm
Liquid											
1	0.900	1.0×10 ³	1.0×10 ³	41.7	2.4×10 ⁶	1.6	1.7	1.5	2.0×10 ²	----	7.7
2	.900	1.0	1.0	25.0	1.4	1.0	.2	1.0	2.1	----	7.7
3	.898	1.0	1.0	25.0	1.4	2.0	.3	.5	4.2	----	26.6
4	.907	.5	.5	33.3	.95	.8	.2	1.0	2.5	----	7.7
5	.905	1.0	1.0	16.7	.95	.9	---	1.0	2.9	----	7.7
Vapor											
6	0.025	1.0×10 ³	0.38×10 ³	25.0	13	2.9	9.1	2.0	6.6×10 ⁷	1020	530
7	.047	1.0	.48	25.0	16	1.8	3.2	2.0	3.5	2050	780
8	.025	1.0	.38	25.0	13	30.6	14.7	.5	70	1020	1890
9	.025	1.0	.38	25.0	13	14.9	10.3	.5	34	1020	1330
10	.025	1.0	.38	41.7	22	4.5	5.7	2.0	6.2	1020	530
11	.015	.1	.084	81.7	12	3.0	---	2.0	7.8	500	300
12	.024	.1	.038	250	13	3.0	---	2.0	7.1	1020	530

^a All irradiations conducted at room temperature, approximately 28° C.

Vapor irradiations conducted under an initial pressure of approximately 13.5 mm Hg, vapor pressure of hydrazine at room temperature.

^b Standard temperature and pressure.TABLE II. - X-IRRADIATION OF 1,1-DIMETHYLHYDRAZINE (UDMH)^a

Experiment	Sample weight, g	Dose rate (meter) r/min	Dose rate (ferrous sulfate solution) r/min	Irradiation time, hr	Dose absorbed by sample, rads	UDMH decomposed, percent	Volume N ₂ +H ₂ formed (STP) ^b , ml	Ratio of nitrogen to hydrogen, N ₂ /H ₂	Values of G for decomposition of UDMH
Liquid									
13	5.96	0.86×10 ³	0.86×10 ³	14.7	5.7×10 ⁵	3.40	0.5	0.5 ↓	9.6×10 ²
14	1.20	.86	.86	19.6	7.5	4.70	1.0		10
15	1.20	1.0	1.0	41.7	19	12.3	2.5		11
16	1.20	1.0	1.0	4.17	1.9	1.31	.3		11
17	1.20	.5	.5	33.3	7.5	4.69	1.1		10
Vapor									
18	0.85	0.94×10 ³	0.48×10 ³	4.5	51	1.0	0.5	1.5	3.1×10 ⁶
19	.85	1.0	.48	41.7	470	5.5	.8	2.0	1.9
20	.86	1.0	.48	4.17	48	.3	.3	.5	1.0

^a All irradiations conducted at room temperature, approximately 28° C.

Vapor irradiations conducted in 2050 cu cm cell under approximately 145 mm Hg, vapor pressure of 1,1-dimethylhydrazine at room temperature.

^b Standard temperature and pressure.

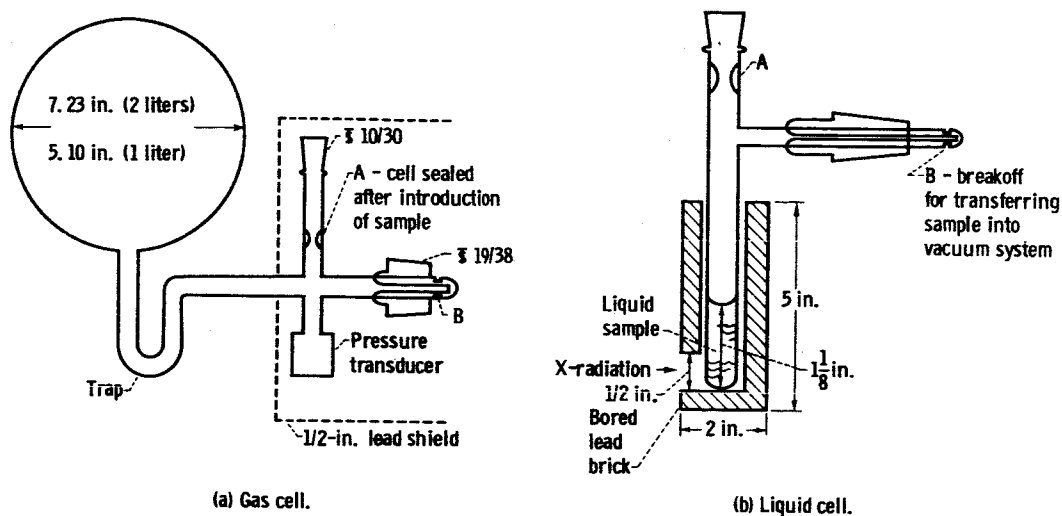
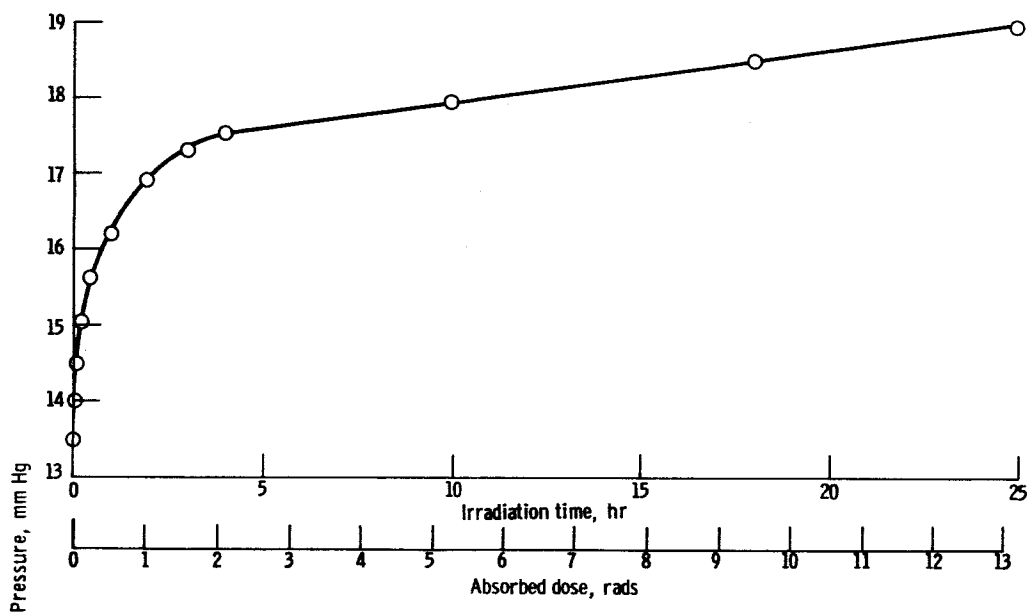
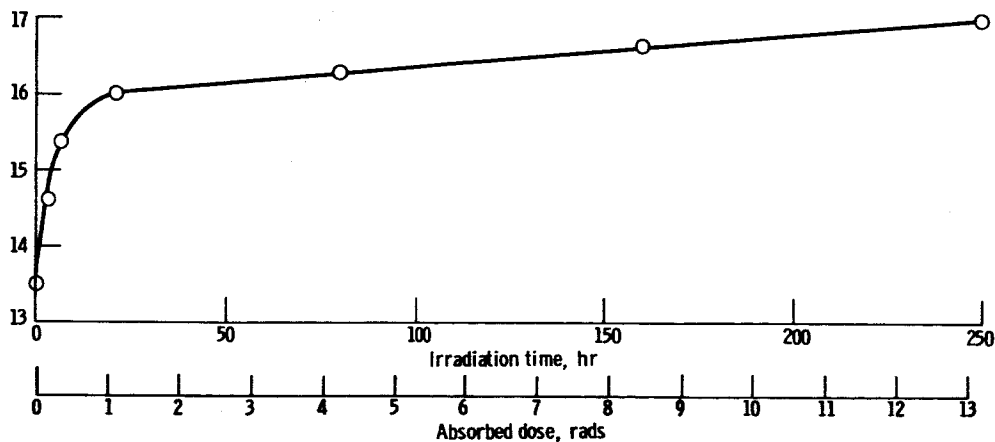


Figure 1. - Borosilicate cells used to irradiate hydrazine and 1, 1-dimethylhydrazine.



(a) Experiment 8; dose rate, 1000 roentgens per minute; cell surface area, 1890 square centimeters.



(b) Experiment 12; dose rate, 100 roentgens per minute; cell surface area, 530 square centimeters.

Figure 2. - X-irradiation of hydrazine vapor. Sample size, 0.025 gram.

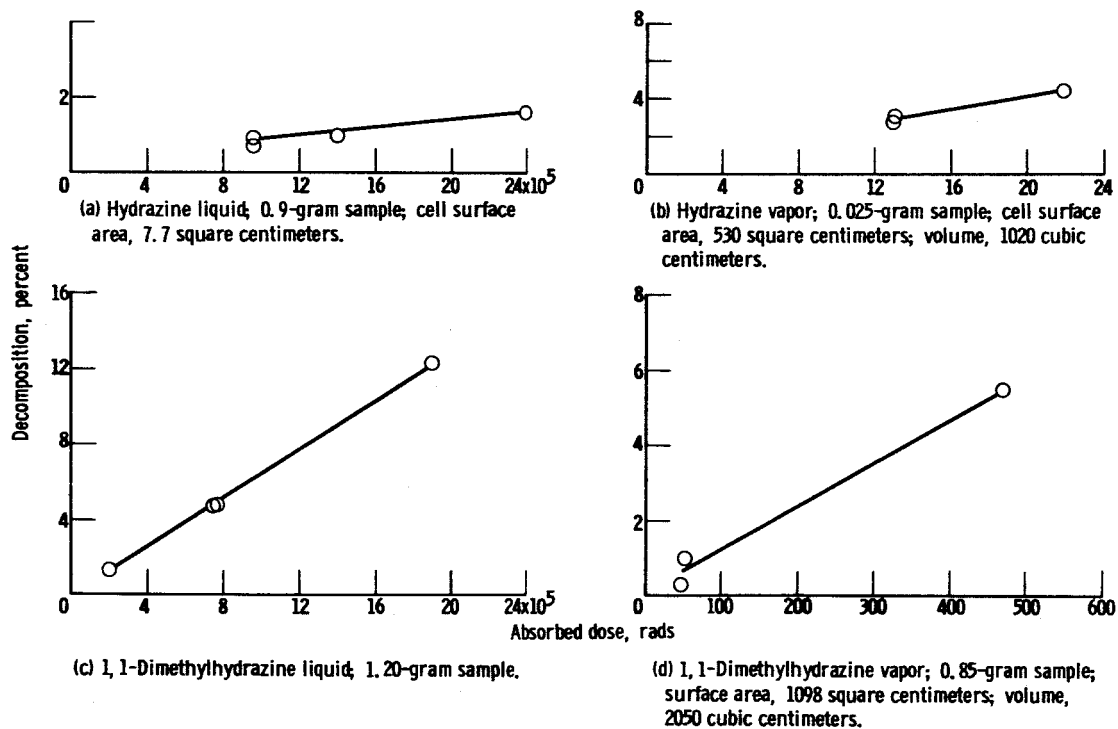


Figure 3. - Effect of size of absorbed X-ray dose on percent decomposition of hydrazine and 1,1-dimethylhydrazine (UDMH).